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Microbially Enhanced Geologic Containment of Sequestered Supercritical CO_2

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Abstract

Geologic sequestration of CO_2 involves injection into underground formations including oil beds, deep un-minable coal seams, and deep saline aquifers with temperature and pressure conditions such that CO_2 will likely be in the supercritical state. It is important that the receiving aquifer have sufficient porosity and permeability and be overlain by a suitable low-permeability cap rock formation. Supercritical CO_2 injected into the receiving formation is only slightly soluble in water (approximately 4%) and therefore two fluid phases develop. Also, supercritical CO_2 is less dense and much less viscous than the initially resident brine resulting in the potential for upward leakage of CO_2 through fractures, disturbed rock, or cement lining near injection wells. This paper summarizes recent research on microbially-based strategies for controlling leakage of CO_2 during geologic sequestration. We examine the concept of using engineered microbial biofilms which are capable of precipitating crystalline calcium carbonate using the process of ureolysis. The resulting combination of biofilm plus mineral deposits, if targeted near points of CO_2 injection, may result in the long-term sealing of preferential leakage pathways. Successful development of these biologically-based concepts could result in a CO_2 leakage mitigation technology which can be applied either before CO_2 injection or as a remedial measure.

Key words Climate change, CO2 sequestration; biofilm; supercritical CO2; porous media permeability

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1.0 Introduction

Active carbon management is required to control the increase in atmospheric carbon dioxide and thereby mitigate the severity of climate change (Pacala and Socolow [18]). One promising management option is geological storage of CO_2, wherein CO_2 is captured before being released to the atmosphere, and then injected via wells into deep geological formations (Kaya [12]; Bachu [1]). Because of the high pressures and temperatures at depth, the injected CO_2 will be in a supercritical state, and the subsequent flow dynamics involve multiple fluid phases in a porous rock matrix. Geological storage is attractive because the technology for injection already exists, and it has already been applied for enhanced oil recovery, acid gas disposal, and deep disposal of hazardous wastes (Donaldson [6]; Moritis [16]; Torp and Gale 22]). However, none of these activities approaches the scale involved in CO_2 injection, where a substantial fraction of the 25 Gt (gigatonnes) of CO_2 produced each year needs to be sequestered away from the atmosphere. In addition, in order to have the desired effects on climate change, the injected CO_2 should stay out of the atmosphere for at least centuries, and preferably for millennia. Likely underground formations for CO_2 sequestration include oil reservoirs, deep un-minable coal seams, and deep saline aquifers with temperature and pressure conditions such that CO_2 will likely be in the supercritical state ($scCO_2$).

When $scCO_2$ is injected into a deep formation, such as deep saline aquifer, it will spread out radially from the well, displacing the resident brine. Supercritical CO_2 is slightly soluble in water, with a solubility limit of about 4% by volume (Enick and Klara [7]), so it forms a separate fluid phase and therefore the system involves two-phase flow. The injected CO_2 will be less dense and much less viscous than the initially resident brine (Nordbotten et al. [17]). This leads to a CO_2 plume that moves radially away from the injection well, while moving progressively higher in the formation, with the invasion front driven by both gravity override and viscous instability.

2.0 Leakage Mitigation a Key Issue

The upward movement of the $scCO_2$ plume will be limited by the low-permeability cap rock that would typically bound the aquifer above. However, if preferential flow pathways exist through the cap rock unwanted upward migration of CO_2 into shallower zones will very likely occur as shown conceptually in Figure 1.

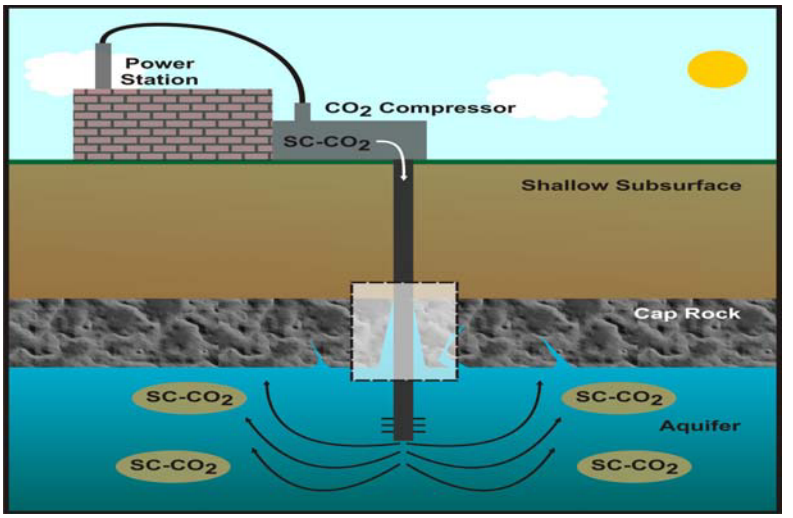


Figure 1. Schematic diagram showing region near the well bore in which the use of microbial biofilms and biomineral deposits may be used to plug leakage flow paths penetrating through cap rock formations.

Fractures in disturbed rock and cement lining near the well bore are very likely to form preferential flow paths. Injection of $scCO_2$ has also been shown to propagate the formation of discrete dissolution features in the host rock, presumably due to the development of acidic brine solutions resulting from the dissolution and disassociation of CO_2 into the residual groundwater in the underground formations. It is therefore imperative to develop methods for mitigating CO_2 leakage as a step toward developing subsurface CO_2 storage as a viable mechanism to reduce concentrations of atmospheric CO_2 (UNEP [23]). This paper focuses on developing strategies for leakage mitigation based on forming microbial biofilm and biomineralization deposits which preferentially plug CO_2 leakage pathways.

3.0 Biofilm Barriers in the Shallow Subsurface

Microbial biofilms have been shown to be effective at plugging pore channels and thereby forming barriers which reduce flow and mass transport through porous media (Cunningham et al.[3]). Conceptually biofilm barrier technology involves the injection of nutrients (i.e. substrate, electron acceptors, trace nutrients) which stimulate growth of bacteria attached to the surface of porous media. Depending on the microbial populations present, it may be desirable to inject bacterial inocula to encourage desired phenotypic expression—such as the production of extracellular polymer substances (EPS). If EPS production can be stimulated along with cell growth, the resulting biomass will plug the free pore space of the aquifer thereby reducing porosity and hydraulic conductivity. (Taylor and Jaffe [21]; Cunningham et al.[4]; Sharp et al.[19]). Engineered biofilm barrier technology has been evaluated at the field scale by Cunningham, et al.[2]. During this 22-month demonstration project a 10 m wide biofilm barrier was developed along the centerline of a 44 m wide, 60 m long, 7 m deep lined outdoor test cell. The barrier was formed by injecting a starved bacterial inoculum of *Pseudomonas fluorescens* strain CPC211a, followed by injection of a growth nutrient mixture composed of molasses, nitrate, and other additives. A 99% reduction of average hydraulic conductivity across the barrier was accomplished after 3 months of weekly or bi-weekly injections of growth nutrient.

4.0 Biofilm-based Strategies for CO_2 Leakage Mitigation

In light of the successful results of biofilm barrier technology in the shallow subsurface the possibility of using a similar approach for CO_2 leakage mitigation is now being explored. A recently published study by Mitchell et al.[13] has examined the process of biofilm formation and associated permeability reduction in rock cores under environmental conditions representative of sites suitable for CO_2 sequestration. This study describes the use of a unique high pressure (<8.9 MPa), moderate temperature (≥ 32 °C) flow reactor containing a 46 millidarcy Berea sandstone core. The flow reactor containing the sandstone core was inoculated with the biofilm forming organism *Shewanella fridgidimarina,* which was recovered from the produced water of an enhanced oil recovery operation. After 825 hours of reactor operation, electron microscopy of the rock core revealed substantial biofilm accumulation in pore channels which resulted in a two order-of-magnitude reduction (approximately 0.4 milidarcys) in core permeability. When the core was challenged with $scCO_2$ for a period of 71 hours the permeability was observed to increase to approximately 4 milidarcys. This study demonstrates that microbial biofilms can be grown under pressures and temperatures representative of environmental conditions in deep subsurface aquifers which can serve as reservoirs for CO_2 storage. The ability to grow biofilms and reduce permeability under these conditions suggests that preferential leakage pathways may be able to be plugged using microbial biomass in a similar manner to the biofilm barriers used in the shallow subsurface. While this concept is interesting and worthy of further exploration we focus now on the use of biofilms to stimulate the precipitation of calcium carbonate which, if formed in abundance, may offer a means of plugging preferential flow paths with both mineral deposits as well as biomass.

5.0 Microbially Enhanced Biomineralization

Biofilm communities in the subsurface are able to actively precipitate calcium carbonate minerals from the ambient Ca^{2+} and HCO_3^- in the subsurface water. However, by stimulating native subsurface microbial communities, or by adding specific microorganisms and growth media, we may be able to engineer the biomineralization process in beneficial ways. One feasible mechanism by which to generate calcium carbonate precipitation in the subsurface is by bacterial hydrolysis of urea, known as ureolysis.

Ureolysis results in the production of ammonium ions (NH_4^+) and carbonate ions, and an increase in pH, which favors calcite precipitation (Ferris et al.[9]). The urease enzyme (urea amidohydrolase; EC 3.5.1.5) responsible for catalysing ureolysis is common in a wide variety of microorganisms (Swensen and Bakken [20]). One mole of urea is hydrolyzed intracellularly to 1 mol of ammonia and 1 mol of carbamate (Eq. 1), which spontaneously hydrolyzes to form an additional 1 mol of ammonia and carbonic acid (Eq. 2). These products subsequently equilibrate in water to form bicarbonate and 2 mol of ammonium and hydroxide ions (Eq. 3 and 4). The latter give rise to a pH increase, which in turn can shift the bicarbonate equilibrium, resulting in the formation of carbonate ions (Eq. 5), which in the presence of soluble calcium ions precipitate as $CaCO_3$ (Eq. 6) (Ferris et al.[8]; Mitchell and Ferris [15]).

$$CO(NH_2)_2 + H_2O \rightarrow NH_2COOH + NH_3 \quad \text{(Eq. 1)}$$

$$NH_2COOH + H_2O \rightarrow NH_3 + H_2CO_3 \quad \text{(Eq. 2)}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \ (pK_{a2} = 6.37) \quad \text{(Eq. 3)}$$

$$2NH_3 + 2H_2O \leftrightarrow 2NH_4^+ + 2OH^- \quad \text{(Eq. 4)}$$

$$HCO_3^- + H^+ + 2OH^- \leftrightarrow CO_3^{2-} + 2H_2O \quad \text{(Eq. 5)}$$

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3 \ (K_{SO} = 3.8 \times 10^{-9}) \quad \text{(Eq. 6)}$$

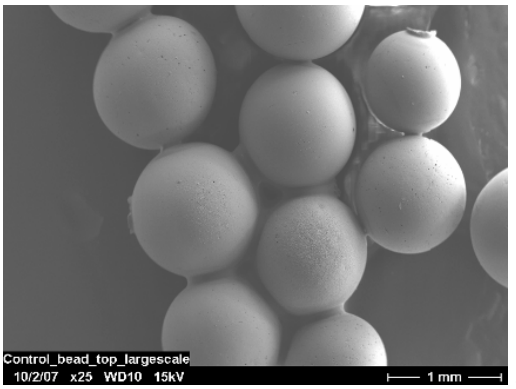
Ureolysis can therefore be readily induced by adding inexpensive urea and has consequently been investigated for industrial utilities such as mineral plugging (Ferris and Stehmeier[10]; Ferris et al.[9]) and immobilizing calcium and contaminants in surface and groundwater (Curti [5]; Hammes et al. [11]); Mitchell and Ferris [14]). Fundamental research into this mechanism using planktonic microbial communities in relation to co-precipitating radionuclides in contaminated vadose zone groundwater has been carried out by Mitchell and Ferris [15;14] specifically determining the temperature and kinetic dependence of ureolysis, and the effect of contaminants and microbial cell surfaces on the mineralogy and morphology of the calcium carbonate precipitated. Ureolysis can occur under dark subsurface conditions and increases bulk solution pH and alkalinity which, in the presence of the common cation Ca^{2+}, can induce the saturation and precipitation of $CaCO_3$—thereby forming a barrier to flow and mass transport in porous media. Many of these studies have utilized planktonic microbial communities, but have not investigated how engineered ureolytic biofilm communities can precipitate calcium carbonate minerals under flow conditions in porous media. Recent experimental results are summarized below.

6.0 Biomineralization in Packed Columns

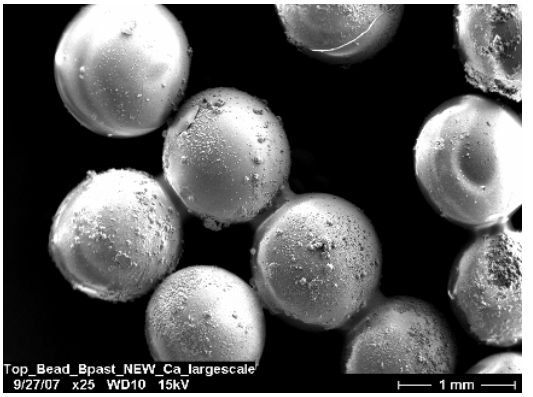
The ability of urea hydrolyzing (ureolytic) biofilms to stimulate $CaCO_3$ mineral formation under non-flowing conditions was investigated in 0.33 m long, 2.54 cm diameter columns containing 1 mm glass beads. The protocol for these experiments was to first inoculate the columns with a known ureolytic bacterium, *Sporosarcina pasteurii* (formerly *Bacillus pasteurii*), add growth medium and develop a biofilm on the surface of the beads. This process took between 2 and 3 days to complete. Once the biofilm was in place, a similar growth medium containing calcium was added to the column to initiate the

biomineralization process. The columns were filled with one pore volume of medium and allowed to remain static for 24 hours before flushing and replacing with another pore volume of fresh medium. The growth medium was made in the following manner: Three grams of Difco Nutrient Broth (BD, Sparks, MD) were dissolved in 500 mL of nanopure water and autoclaved for 25 minutes. 20 grams of Urea (Fisher, Fair Lawn, NJ), 10 grams of ammonium chloride (Fisher, Fair Lawn, NJ), and 2.1 grams of sodium bicarbonate (Fisher, Fair Lawn, NJ) were dissolved in 500 mL of nanopure water on a stir plate. This solution was added to the nutrient broth after it had cooled to room temperature. The whole solution was adjusted to pH 6 +/- 0.1 using concentrated HCl. For calcium inclusive medium, 3.7 grams of calcium chloride dihydrate (Acros, NJ, USA) were added after pH adjustment. The complete medium was filter sterilized using a SteriTop (Fisher, Fair Lawn, NJ) 0.22 µm vacuum filter.

Stereoscope images of 1 mm glass beads with the resulting biofilm and mineral deposits are shown in Figures 2. In Figure 2a the *S. pasteurii* biofilm is visible on the exposed edges of the beads. Note that the biofilm coverage is relatively thin over most of the bead surface with occasional locations of higher accumulation in the pore throats. Figure 2b shows 1 mm beads after 14 days of exposure to biomineralizing conditions.

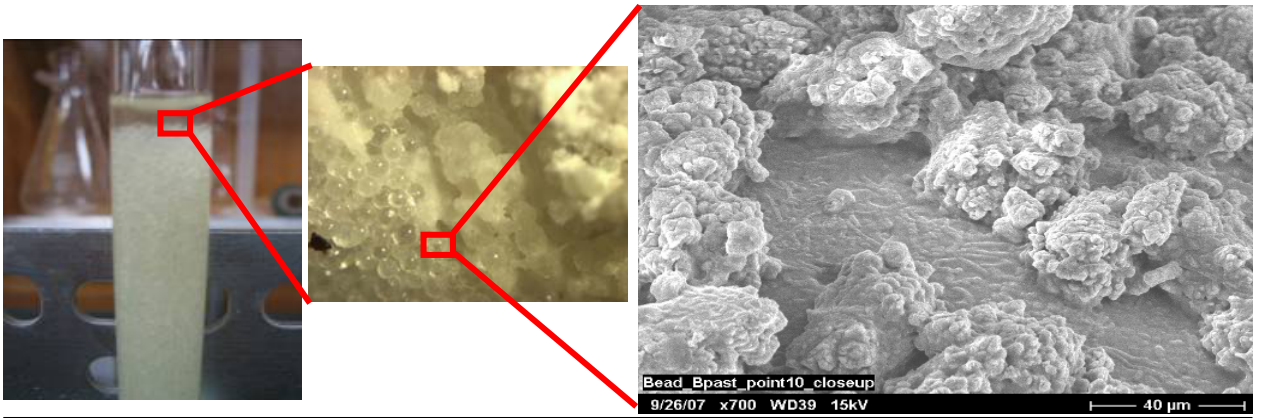


a)



b)

Figure 2a. Biofilm deposits *(S. pasteurii)* on 1mm glass beads prior to onset of biomineralization. Biofilm accumulation is clearly visible in the pore throats between beads. **Figure 2b.** 1mm beads 14 days after biomineralization was initiated.



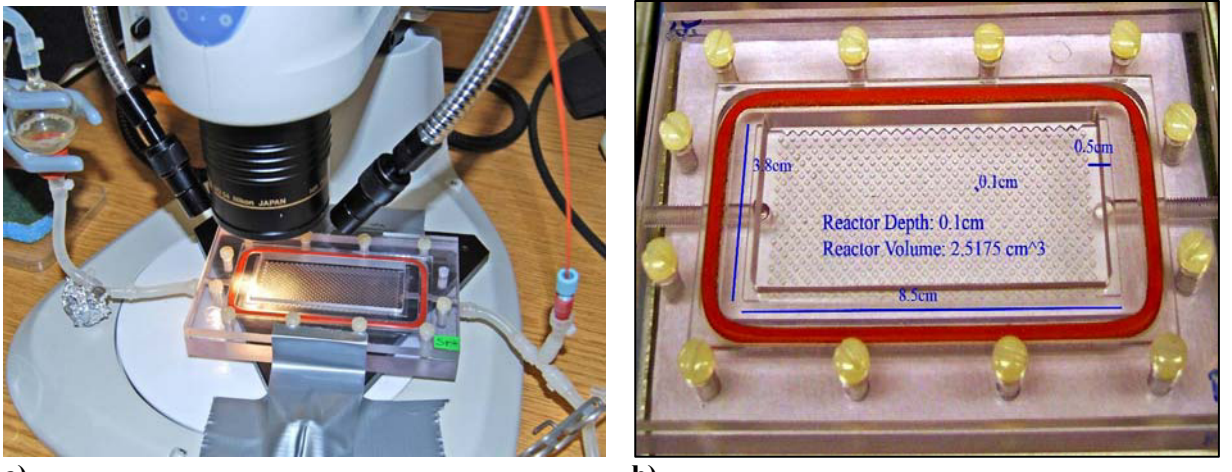
c)

Figure 2c. Scanning electron Microscope image (SEM) showing calcium carbonate deposits on top of ureolytic biofilm cells after 14 days of column operation. Note the relatively large mass of calcite deposits compared to the mass of the biofilm cells.

Figure 2c shows the bead surface after 14 pore volumes (14 days) of biomineralizing solution have passed through the columns. These Scanning Electron Microscope (SEM) images show the *S. pasteurii* biofilm cells on the bead surface surrounded by relatively large deposits of calcium carbonate. The important observation here is that relatively large quantities of mineral can be deposited from the biomineralizing activity of relatively few biofilm cells. Our hypothesis is that calcium carbonate will continue to be deposited for as long as *S. pasteurii* cells remain active. It was also observed that the biofilm-mineral deposits in the 1 mm glass bed were not of sufficient size to cause any measurable plugging of the column. However, when these experiments were repeated using 0.1mm glass beads the biofilm-mineral deposits resulted in complete plugging of the column (i.e. the columns would not drain under gravity flow conditions).

7.0 Biomineralization in flowing systems

The process of ureolytic biomineralization was next investigated under continuous flow conditions using the 8.5 cm x 3.8 cm flat plate polycarbonate reactor flow system shown in Figure 3. The polycarbonate surface was etched with 1 mm x 1mm diagonal flow channels thereby creating a tortuous flow through the reactor. A flow rate of 0.15 ml/min was initiated which resulted in a hydraulic detention time of 16.8 min. Initially the reactors were inoculated with S. *pasteurii* and a "no flow" condition was maintained for 3 hours. At this point a constant flow of growth medium (same composition as previously described) was begun.



a) **b)**

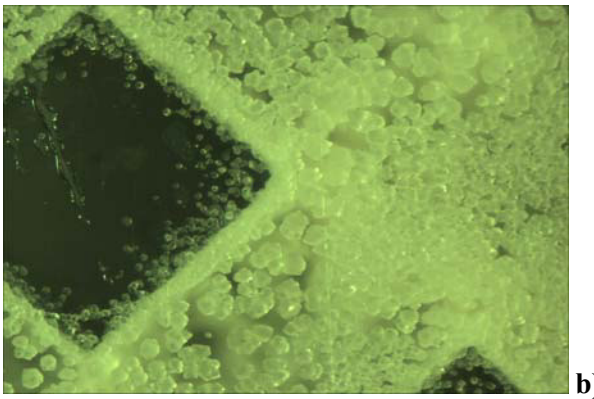
Figure 3a. Stereoscope system for observing biomineralization deposits on roughness elements inside flow cell. **Figure 3b.** Close up of flow cell reactor showing etched roughness element pattern which results in tortuous laminar (porous media) flow inside the 2-dimensional flow field. Flow is from left to right through the reactor.

Although these experiments were intended to be run using a constant flow rate, it was necessary to reduce the flow rate after mineral deposits began to form in order to minimize excess pressure buildup at the entrance to the reactor. After approximately 20 hours of operation a "no flow" condition was reached as the reactor had become completely plugged with calcium carbonate crystals (Figure 4).

Stereoscopic analysis of the biofilm-calcium carbonate deposits in Figure 4 reveals that a significant gradient in deposit mass occurred along the flow path through the reactor. This observation suggests that one or more constituents required for biomineralization to occur were limiting the deposition process

along the flow path. Future experiments will be directed toward identifying the causes of depositional rate limitation.

a)



b)

Figure 4a. Flat plate reactor after 20 hours of operation showing complete plugging with calcium carbonate deposits. **Figure 4b**. Close-up of calcium carbonate deposits blocking the 1mm flow channels near reactor inlet.

8.0 Summary

Recent experiments show that engineered biofilms, grown at 8.9 MPa and 35^{O} C, can reduce permeability in rock cores and withstand short-term challenges by scCO_2. Additional experiments demonstrate the possibility of developing engineered biofilms in porous media which result in precipitation of calcium carbonate using the process of ureolysis. The resulting combination of biofilm plus mineral deposits, if targeted near points of CO_2 injection, may result in the long-term sealing of preferential leakage pathways. Successful development of these biologically-based concepts will result in a CO_2 leakage mitigation technology which can be applied either before CO_2 injection or as a remedial measure.

9.0 Acknowledgements

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